



NO DRAWINGS

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COMPLETE SPECIFICATION

Dehydrogenation of Aliphatic Hydrocarbons and Catalyst therefor

We, AIR PRODUCTS AND CHEMICALS, INC., a Corporation organised and existing under the laws of the State of Delaware, United States of America, of 1528 Walnut Street, Philadelphia, State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the dehydrogenation of hydrocarbons, particularly of aliphatic hydrocarbons having 3 to 5 carbon atoms, and is particularly concerned with the provision of improved catalyst for use in such processes.

Chromia-alumina catalysts have been extensively employed in dehydrogenation as well as in other hydrocarbon conversion processes. The catalysts principally suggested for use in dehydrogenation of C_3 to C_5 aliphatic hydrocarbons are those containing 3 to 30% or more Cr_2O_3 with or without added other metal oxide promoters, supported on a porous alumina carrier such as activated alumina. In commercial practice the dehydrogenation of butane to butylene and/or butadiene has been largely carried out in a fixed catalyst bed system employing a battery of reactors in timed cycles such that each bed of catalyst, after a short period of on-stream hydrocarbon conversion, is subjected to regeneration for combustion of the accumulated coke. The catalyst employed in these commercial operations generally comprises 18 to 20% chromic oxide by weight of the catalyst in association with pelleted alumina.

In typical commercial operations for production of butadiene from a butane feed containing recycled butylenes (which may be all or part of the mono-olefins produced in the process) the dehydrogenation is carried out at about 593°C. and at sub-atmospheric pressure of about 245 grams /sq. cm. absolute, with on-stream periods of 5 to 10 minutes. Typical

effluent from an operation charging a hydrocarbon stream containing about 73 volume % n-butane and 27 volume % recycled butylenes, contains 10% butadiene, 40% butylenes and 39% unconverted butane. In some operations all or the major part of the butylenes produced are recovered for use in alkylation or other desired uses; here the recycle stream will contain no more than about 5% butylenes. Typical effluent yields in such operation contain about 6% butadiene and about 31% butylenes.

In accordance with the present invention the dehydrogenation of C_3 to C_5 hydrocarbons is considerably enhanced by the use of novel chromia-alumina catalysts of higher activity and by operating the process at selected conditions particularly adapted to such novel catalysts. By the operation for dehydrogenation of butanes for example, in accordance with the invention, exceptionally high yields of butylenes are obtained. Moreover, if desired, high yields of butadiene can be achieved by recycling product streams of high butylene content. In similar manner dehydrogenation of isopentane by the method described obtains high yields of isopentane, which can be recycled for ultimate good production of isoprene. Good dehydrogenation of propane to propylene is obtained with the present catalyst at lower temperatures than those required for available commercial chromia-alumina catalysts.

In accordance with the present invention, there is provided a method of preparing a catalyst useful for dehydrogenating C_3 to C_5 hydrocarbons, which comprises dehydrating an alumina hydrate composition containing at least 60%, preferably 70 to 100%, beta alumina trihydrate, heating the resulting dehydrated alumina with a stream of gas comprising steam to adjust the surface area thereof to the range of 100 to 200 square meters per gram, depositing chromia on the area adjusted dehydrated alumina to provide a catalyst comprising 10 to 25% Cr_2O_3 and after incorpora

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tion of the chromia again treating the catalyst at elevated temperature with a stream of gas comprising steam.

The catalyst preferably contains a small amount of combined alkali metal associated therewith, e.g. in the range of 0.2 to 1.2% Na_2O .

The present invention also provides a method of dehydrogenating C_3 to C_8 hydrocarbons by passing a charge comprising such hydrocarbons over the catalyst prepared by the above method.

The novel catalysts of the invention can be used—and preferably are used—at lower temperatures than those heretofore advocated for best practical operation in dehydrogenation of C_3 to C_8 hydrocarbons. Such lower operating temperatures afford important savings in structural and maintenance costs as well as in utility requirements. Thus, such lower operating temperatures result in decreased rates of corrosion at the valves and other critical parts of the apparatus, permit lower preheating temperatures for the charge hydrocarbons with consequent lower yield loss from thermal cracking, and decrease the possible extent of temperature variation among reactors. Moreover, greater flexibility of operation is afforded from the standpoint of being enabled to supply, by appropriate heating of the hydrocarbon charge, the desired portion of required heat for the endothermic hydrocarbon conversion.

It has now become recognized in the art that catalysts having the same chemical composition, so far as can be determined by ordinary analytical methods, may vary widely in properties, depending upon the particular manner in which the catalyst has been prepared. It has been found, for example, that in alumina-supported catalysts, wide differences in properties can be expected as a result of variations in the manner of preparing the alumina support with which the active catalytic component is associated.

Alumina occurs or can be produced in various structural forms and in different phases of hydration. Among the hydrated forms of alumina there are distinguished:

(a) Alpha alumina trihydrate corresponding to the mineralogical designations gibbsite and hydrargillite. This form occurs naturally or is readily prepared synthetically by known procedures. This is generally regarded as the form of alumina obtained by the Bayer process.

(b) Beta alumina trihydrate, corresponding to the mineralogical designation bayerite. It can be synthetically prepared by controlled aging of precipitated boehmite under cold alkaline conditions. On further extended aging bayerite is gradually transformed to gibbsite. A dense form of alumina beta trihydrate is obtained by CO_2 precipitation of sodium aluminate solution and a somewhat lighter

form of beta trihydrate of higher surface area is obtained by alkaline hydrolysis of aluminum alcoholates or the action of water on amalgamated aluminum metal.

(c) Alpha alumina monohydrate corresponding to the mineralogical designation boehmite. It can be prepared simply by adding ammonium hydroxide to an aqueous solution of aluminum chloride. The original gelatinous precipitate rapidly increases in crystallite size to form the crystal structure identified as boehmite.

(d) Beta alumina monohydrate, known mineralogically as diasore, occurs abundantly in nature.

Considerable confusion exists in the art as to the structural changes which take place on heating various forms of hydrated alumina. The designation eta alumina has been applied by most investigators [see Stumpf et al.: *Ind. Eng. Chem.*, Vol. 42, p. 1398 et seq. (1950)] to the transitional form of alumina which begins to appear when beta alumina trihydrate is heated for 1 hour in air at temperatures above about 250°C . By extended heating in dry air at temperatures in excess of about 960°C . or in steam above 780°C ., eta alumina is stated to show a tendency toward transformation to a next structural stage called theta alumina. Accordingly without attempting to name more precisely the structural or crystalline forms or phases present, the catalyst of the invention can be identified as comprising as carrier the activated alumina product obtained by dehydration of a hydrated alumina composition containing at least 60% and preferably no less than 70% beta trihydrate.

EXAMPLE I

(a) High purity bayerite powder (96+ % beta trihydrate) was thoroughly admixed by mulling with aqueous nitric acid employing 0.09 parts nitric acid (1.42 SG) and 0.108 water by weight of the alumina trihydrate. The acid mix after standing overnight was extruded through a die plate and the strands cut to form 2.4 mm pellets. The pellets were dried at 116°C . for 2 hours and then calcined in air for one hour at 427°C . (surface area = $367\text{ m}^2/\text{g}$). The calcined pellets were then subjected to surface area adjustment by steaming (100% H_2O) for 2 hours at 482°C . (surface area = $190\text{ m}^2/\text{g}$).

(b) An aqueous solution of chromic acid was prepared by dissolving 945 grams of CrO_3 in water to form 1.5 liters of solution, which solution was used to impregnate a portion of the area-adjusted alumina pellets from (a) above using sufficient solution to give 945 grams CrO_3 per 1200 grams Al_2O_3 . The pellets were permitted to soak in the solution overnight. The soaked pellets were then decanted, dried and calcined at 699°C . in flowing oxygen (surface area = $102\text{ m}^2/\text{g}$). Analysis of the calcined pellets (ignited basis) showed $22.13 \pm .08\%$ by weight Cr_2O_3 .

This catalyst was tested for dehydrogenation of butane under standard conditions (593°C., LHSV=1, and at 127 mm. Hg absolute pressure) but was found to be too active for practical use. The catalyst produced 25% coke by weight of charge at an 85% total hydrocarbon conversion level. Extensive cracking of the charge was evidenced by the yield of 24% by weight of C₁—C₃ hydrocarbons.

In an attempt to reduce the high cracking activity of the catalyst, a number of experiments were carried out in which, respectively:

(a) Alkali metal ion was added to the catalyst to give 0.5% and 1.0% Na₂O, respectively.

(b) Each of the catalyst from (a) above was subjected to severe thermal deactivation by treatment with steam and hydrogen at 871°C. for six hours, in some instances with additional air calcination.

These catalysts were then tested under standard conditions in dehydrogenation of butane, obtaining results as reported in Table 1 below.

TABLE 1

| Cat. | Wt. % Chg. | | Butenes | | Butadiene | | Total Dehydro Select. | C ₁ —C ₃ Wt. % Chg. |
|------|------------|------|---------|---------|-----------|---------|-----------------------|-------------------------------------------|
| | Conv. | Coke | Wt. % | Select. | Wt. % | Select. | | |
| (a) | | | | (b) | | (c) | (b + c) | |
| 1 | 85 | 25 | 20 | 24 | 10 | 12 | 36 | 24 |
| 2 | 87 | 22 | 21 | 24 | 12 | 14 | 38 | 25 0.5 Na ₂ O |
| 3 | 60 | 3.5 | 33 | 55 | 14.5 | 24 | 79 | 6.7 " |
| 4 | 70 | 7.1 | 34 | 48 | 16.2 | 23 | 71 | 9.4 " |
| 5 | 65 | 5.5 | 34 | 52 | 14.0 | 22 | 74 | 7.8 " |
| 6 | 64 | 2.9 | 34 | 53 | 16.7 | 26 | 79 | 7.3 1.0 Na ₂ O |
| 7 | 26 | 0.2 | 17 | 66 | 3.5 | 14 | 80 | — ca. 0.5 Na ₂ O |

(a) Catalysts.

(1) Example I.

(2) Prepared similarly to Example I but with incorporation of 0.5% by weight Na₂O in the chromia impregnating solution, using Na₂CrO₄ for part of the CrO₃.

(3) Same as (2) but further calcined after the run above, by treatment for six hours at 871°C. in hydrogen plus steam (80% H₂).

(4) Catalyst from (3) after the run further treated in air for 20 hours at 604.4°C.

(5) Fresh catalyst prepared as in (2) above, but calcined after chromia impregnation, for

6 hours at 871°C. in 20% steam, 80% hydrogen (surface area = 80 m²/g).

(6) Prepared similarly to (2) but with inclusion of 1.0% Na₂O ex sodium chromate. The impregnated pellets were calcined in air for 16 hours at 660°C., then further treated in hydrogen and steam (80—20) for six hours at 871°C.

(7) Commercial 3.2 mm chromia-alumina dehydrogenation catalyst, hydrogen and steam treated at 829.4°C. for 2 hours.

$$(b) \text{ Selectivity (butenes)} = \frac{\text{wt \% net butenes produced}}{\text{wt \% butane disappearance}} \times 100$$

$$(c) \text{ Selectivity (butadiene)} = \frac{\text{wt \% net butadiene produced}}{\text{wt \% butane disappearance}} \times 100$$

The above runs indicate that extensive reduction in coke-making potential was achieved by the thermal deactivation treatment, and that

these catalysts had exceptional thermal stability.

Chromia-alumina catalysts commercially

employed in dehydrogenation of aliphatic hydrocarbons are prepared by impregnation of activated alumina obtained by calcination of alpha alumina trihydrate. In typical commercial practice for dehydrogenation of butane in a fixed catalyst bed under adiabatic conditions, the operation is generally carried out at about 593°C. average bed temperature or somewhat higher. To maintain the reaction temperature at about 593°C. in systems operated for high butadiene yields with recycling of butylenes, a hydrocarbon inlet temperature of about 593°C. may be employed with the catalyst bed temperature varying generally from 599°C. to 610°C. at the hot regions to 571°C. to 588°C. at the cooler regions. In operations designed for maximum butylene yields and recovery of produced butylenes (not recycled) about the same feed temperature of the butane would be employed with the average catalyst bed temperatures approximating or somewhat below the feed temperature. Typical once-through yields from normal butane dehydrogenation with the best of the available commercial catalysts will average (weight per cent of charge) about 31—32% butylenes and 6 to 8% butadiene at about 45 to 50% butane conversion (80% selectivity), the remainder being chiefly gas and coke. By the use of the catalysts of the present invention, the yields of butenes per pass can be increased by about 50% or more as compared with operations heretofore with the best commercial chromia-alumina catalysts in use. Moreover, these higher yields are obtained advantageously at lower temperatures than those required for optimum operation with present commercially used catalysts. With the comparatively high butylene production characterizing the new catalyst, it is also of beneficial advantage in operations designed for maximum butadiene production, since in such recycle operation the resulting equilibrium feed of higher butylenes content would obtain enhanced butadiene yields per pass.

EXAMPLE II

In preparation of the catalyst used, area-adjusted alumina pellets (820 g/liter density) were produced as in Example I(a) above (190 m²/g surface area). These pellets were soaked in a cooled aqueous solution containing 624 grams/liter CrO₃ and 25 grams/liter NaOH, using 1 liter of solution for each 750 grams of pellets; being sufficient solution to adequately cover the pellets. After 2 hours, the liquid excess was drained and the impregnated pellets dried at 121°C. for about 2 hours. The pellets comprised: nominally 79% Al₂O₃, 20% Cr₂O₃, 1.0% Na₂O, all by weight.

These pellets were heat treated at 760°C. for 4 hours in a steam-air atmosphere containing 20 volume per cent H₂O.

EXAMPLE III

(a) A sodium-containing commercial hydrated alumina powder comprising about 75% beta trihydrate and 25% alpha trihydrate was milled with aqueous nitric acid using for each kilogram of the alumina hydrate 0.09 kilogram of nitric acid (42 Be) and 0.108 kg of distilled water. The mix was formed into 4.0 mm pellets, and the pellets were heat treated in a bomb for 2 hours at 482°C. in air followed by four-hour treatment in 100% steam at 760°C. After steam treatment the pellets had a surface area of 110 m²/g.

(b) The calcined pellets after cooling were impregnated with aqueous chromic acid solution containing 485 grams/liter CrO₃, using 1 liter of solution for each 700 grams of pellets. After the pellets had soaked in the chromic acid solution for 2 hours, the liquid was drained and the pellets dried in air for 2 hours at 121°C.; then calcined for four hours at 760°C. in an atmosphere of 80% air (vol) and 20% steam.

EXAMPLE IV

The catalysts of Example II and III above were used in dehydrogenation of butane in an isothermal reactor at the conditions and with the results reported in Table 2 below.

TABLE 2
Operation at 127 mm Hg Absolute Pressure

| Catalyst | Example II | | | | | | Ex. III | Commercial (a) |
|--------------------------------------|------------|------|------|------|------|------|---------|-------------------|
| Temp. °C. | 588 | 582 | 538 | 632 | 507 | 504 | 593 | 593 |
| Space Rate v/hr/v | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 1 |
| Conv. wt. % | 81.3 | 61.9 | 68.5 | 49.0 | 41.2 | 29.1 | 74.2 | 54.9 |
| Butenes wt. % | 29.2 | 29.9 | 47.2 | 35.8 | 34.0 | 23.9 | 38.4 | 31.4 |
| Butadiene wt. % | 15.9 | 15.0 | 10.4 | 7.8 | 4.0 | 3.3 | 18.3 | 13.1 |
| Coke wt. % | 12.1 | 6.0 | 2.9 | 1.2 | 0.8 | 0.4 | 5.2 | 1.7 |
| C ₁ -C ₃ wt. % | 19.3 | 8.5 | 5.5 | 2.4 | 1.4 | 0.8 | 8.4 | 6.2 |
| Total Select., % by wt. | 55.5 | 72.5 | 84.1 | 89.0 | 92.2 | 93.4 | 76.5 | 81.0 |

(a) Same commercial catalyst (3.2 mm pellets) as No. 7 in Table 1.

The unusual characteristics of the catalysts of the invention will be appreciated when observing the uniquely high yields of mono-olefins and of total C₄ unsaturates that are obtained therewith, the latter amounting to over 55% by weight of charge. Neither in commercial experience nor in any of the numerous experimental catalysts investigated over a wide range of operating conditions, have we encountered any previous catalyst capable of giving such high yields of unsaturates at any selected combination of operating variables. Moreover, it should be noted that these high yields can be obtained at comparatively low temperatures and practical space rates, which factors weigh heavily in the consideration of the economics of the process, not only from the standpoint of reduced utility costs and lower unit upkeep costs alone, but more importantly from the standpoint of expected longer catalyst life. The rate of loss of catalyst activity increases with increase in temperature. Moreover, as the catalyst loses activity the operating temperature is raised to compensate, in order to maintain desired conversion and/or yield. By starting operation with fresh catalyst at lower temperature, the extent to which the

temperature can be raised to a practical maximum temperature during the life of the catalyst, is thus broadened.

EXAMPLE V

(a) A series of runs was carried out in an adiabatic fixed bed reactor loaded with a mixture of 60% by volume catalyst and 40% tabular alumina added as inert heat capacity material. The catalyst employed was prepared using the same beta trihydrate base and by the method described in Example II. The surface area of the dehydrated alumina after area adjustment by 100% steam treatment at 482°C. for 2 hours, was about 183m²/g. Impregnation of the pelleted alumina with chromic acid solution and sodium hydroxide was in accordance with Example II. The chromia-alumina catalyst pellets were given a final heat treatment at 760°C. for 10 hours in 20% steam 80% air and then for an additional 10 hours at that temperature in 20% steam 80% hydrogen.

(b) The charge to the unit was substantially pure butane (99.12% nC₄) which was charged at operating conditions specified in Table III below, obtaining the results there reported:

TABLE 3

| Run | A | B | C | D | E | F | G |
|------------------------------|-------|-------|-------|-------|-------|-------|-------|
| Press. mm. Hg. abs. | 177.8 | 177.8 | 177.8 | 381 | 762 | 762 | 762 |
| Space Rate V/Hr/V | 1.4 | 1.4 | 1.4 | 1.3 | 2.4 | 2.0 | 1.3 |
| Temp. °C. | | | | | | | |
| inlet | 565.6 | 590.6 | 607.2 | 579.4 | 581.0 | 579.4 | 578.5 |
| avg. bed | 529.5 | 545.5 | 568.5 | 544 | 533.3 | 541.1 | 548.9 |
| (1) | 538.9 | 566.7 | 618.3 | 557.4 | 547.8 | 553.3 | 572.2 |
| outlet (2) | 521.1 | 542.3 | 581.1 | 540.6 | 526.7 | 538.9 | 558.9 |
| Conversion (wt. % charge) | 39 | 65.8 | 76.0 | 59.4 | 45.6 | 50.2 | 52.7 |
| Butenes | 30.2 | 47.5 | 44.6 | 46.1 | 37.1 | 40.0 | 38.1 |
| Butadiene | 4.6 | 9.3 | 14.1 | 4.9 | 2.1 | 2.3 | 2.7 |
| Coke | 0.6 | 1.0 | 2.8 | 1.0 | 0.5 | 0.5 | 1.2 |
| Gas Grav. (air = 1) | 1.35 | 1.03 | 0.88 | 1.12 | 1.34 | 1.28 | 1.19 |
| Total Selectivity % | 89.2 | 86.3 | 77.2 | 85.9 | 85.0 | 84.2 | 77.4 |

(1) Temp. at beginning of on-stream.

(2) Temp. at end of on-stream.

5 In comparison with the results reported in column B above, operation under approximately the same conditions of temperature (554.5°C. average outlet), pressure and space rate, typical results obtained with fresh commercial chrome-alumina dehydrogenation catalyst average:

| | Wt. % of Charge |
|-------------------|-----------------|
| 10 Conversion | 38.5 |
| Butenes | 26.6 |
| Butadiene | 5.6 |
| Coke & Gas | 6.3 |
| Total Selectivity | 83.6 |

15 In other words by the use of the catalyst of the invention there is obtained at the same operating conditions over 75% increase in total unsaturates production, and an increase of over 30% in the quantity of butadienes produced.

20 If the temperature of the operation (average outlet bed temperature) using the commercial catalyst is increased to 598.9°C., to corre-

spond to the more usual conditions employed in commercial practice for such catalyst, and maintaining the space rate at a value to obtain approximately the same level of conversion as in the lower temperature operation with the new catalyst of the invention, the yield of desired products is still significantly below that obtained with the latter.

It will be further apparent from Table 3 that desirably high conversion and good selectivity was obtained in Run B at 1.4 space rate and at an average bed temperature of 545.5°C. At the same space rate with increase of average bed temperature to above bed temperature to above 565.6°C. (Run C) there was a significant increase in butadiene make and a slight increase in the total quantity of C₄ unsaturates obtained but only at a significant sacrifice in selectivity. With average bed temperatures approaching around 565.6°C. a somewhat higher space rate accordingly may be preferred.

The runs in columns D to G illustrate the

effect of increased pressure. To maintain desired total selectivity higher space rates are generally indicated with increasing pressure. The higher pressure operation is economically desirable particularly for butylenes production, notwithstanding the somewhat reduced yields.

5 The general conditions of operation for conversion of C_4 and C_5 hydrocarbons at which the noted advantages of the high activity catalyst used in accordance with the present invention are best evident, lie in the range of 10 515—610°C. depending upon the hourly liquid volume space rate employed between 0.5 to 4, such that the minimum (average bed) temperature of the range is at 510°C. plus 11 15 time the hourly liquid volume space rate and the maximum (average bed) temperature of the range is at 554°C. plus 14 times the hourly liquid volume space rate.

20 For conversion of propane or isobutane higher temperatures are advocated as in the range of 593.3 to 621.1°C. at a space rate of one. In particular when the hydrocarbon charge is composed predominantly of propane, 25 the dehydrogenation thereof is preferably effected at temperatures in the range of 593—635°C.

30 In general for operations designed for once through passage (no recycle) in the dehydrogenation of butane, the preferred conditions of operation with the highly active catalyst of the invention include average bed temperatures in the range of about 527 to 565°C., an hourly

liquid volume space rate of 1 to 2 volumes of butane (as liquid) per hour per volume of catalyst and an absolute pressure of 210 to 280 grams per square centimeter, with the space rate being increased within the specified range as the temperature is increased. Under these ranges of conditions there are obtained per pass up to 55% or somewhat greater percentage of total C_4 unsaturates with, e.g., 5—13% of the charge going to butadiene.

When the hydrocarbon charge consists substantially of C_5 hydrocarbons including isopentane, the dehydrogenation conditions preferably include subatmospheric pressure and temperature in the approximate range between 510°C. + 11 SR to 540°C. + 14 SR in which SR is the hourly liquid volume space velocity.

EXAMPLE VI

The same catalyst as in the preceding example (Example V) was employed in several sets of runs involving recycle of produced butylenes, in the quantities and operation under the temperature conditions set out in Table 4 below. For this type of operation a higher ratio of inert heat capacity material to catalyst is desirable for heat balance, so the bed loading employed was 36% catalyst and 65% inert material. The inert material was fused alumina grains having substantially no catalytic activity and commercially marketed under the name Corhart grain. These runs were made at 2.5 liquid hourly space velocity and at a pressure of 178 mm Hg absolute.

TABLE 4

| | | wt. % | | |
|------------------------------------------------------------|-------|-----------------|-------|--|
| Composition of Feed: | | n-butane | 55.6 | |
| | | n-butylene | 43.4 | |
| | | butadiene | 0.1 | |
| | | iC ₄ | 0.4 | |
| Run | H | I | J | |
| Temp., °C. | | | | |
| inlet | 551.7 | 565 | 576.7 | |
| avg. bed | 541.7 | 546.7 | 564.7 | |
| (1) | 557.8 | 573.4 | 601.1 | |
| outlet | | | | |
| (2) | 543.3 | 552.2 | 575.6 | |
| Product effluent, wt. % chg. | | | | |
| butane | 42.0 | 37.6 | 30.5 | |
| butylenes | 42.1 | 43.3 | 44.2 | |
| butadiene | 11.1 | 12.9 | 16.2 | |
| iC ₄ | 0.3 | 0.3 | 0.2 | |
| coke | 1.0 | 1.3 | 2.1 | |
| C ₁ —C ₃ | 2.1 | 2.9 | 4.2 | |
| Conversion, wt. % (nC ₄ + nC ₄ =) | 14.9 | 18.1 | 24.3 | |
| Butadiene Select., wt. % | 74.5 | 71.2 | 66.1 | |

For the same feed composition of Example alumina catalyst give typically the following
VI, operations with commercial chromia- yields:

| | K | L | M | N |
|----------------------------------|---------------------------------------------|-------------------------------------------|---------------------------------------------|-------------------------------------------|
| | at same avg. outlet temp. as column H | at same conv. and temp. as column H | at same avg. outlet temp. as column J | at same conv. and temp. as column J |
| | (550.6° C.) | (Space rate=1.3) | (585.3° C.) | (Space rate=0.72) |
| Product effluent (wt. % chg.) | | | | |
| Butane | 46.3 | 42.0 | 37.3 | 30.5 |
| Butylenes | 40.1 | 43.8 | 39.7 | 46.4 |
| Butadiene | 8.6 | 8.7 | 14.1 | 13.7 |
| Butadiene Selectivity | 68.3 | 65.0 | 64.0 | 62.0 |

Here again, in the recycle operation designed for ultimate butadiene production, the operation of the invention permitting lower temperatures and/or higher space rates, shows important advantages over typical commercial operations.

For dehydrogenation of isopentane with best yields of isoprene the space rates employed and the catalyst/inert loadings are substantially like those utilized in the described C_4 recycle operation for butadiene production, with the temperatures running at about 14°C. lower in the case of the C_5 's and the preferred pressure being at 175 grams per square centimeter absolute or less.

EXAMPLE VII

A series of runs were made over the used catalyst of Example II in an isothermal reactor charging isopentane at 125 mm Hg absolute pressure and at the temperatures and space rates reported in Table 5 below, wherein the results are indicated and compared with commercial chromia-alumina catalyst.

TABLE 5

| Catalyst | Example II after use (2.4 mm size) | | | Commercial (3.2 mm size) | | |
|----------------------|---------------------------------------|------|------|-----------------------------|------|------|
| Temp. °C. | 593.3 | | | 548.9 | | |
| Space Rate V/Hr/V | 1 | 2 | 4 | 1 | 2 | 4 |
| Yields wt. % | 78.1 | 63.9 | 46.8 | 68.4 | 56.0 | 41.4 |
| Conversion | | | | | | |
| iC_3 Mono-olefins | 24.4 | 23.0 | 19.4 | 35.5 | 30.8 | 23.6 |
| iC_3 Diolefins | 13.1 | 13.9 | 11.6 | 8.9 | 9.1 | 8.4 |
| Coke | 18.2 | 10.0 | 5.1 | 7.9 | 4.7 | 2.5 |
| Total Selectivity | 48.0 | 57.8 | 66.2 | 64.8 | 71.3 | 77.2 |

It appears from the foregoing that at the lower temperatures of operation made possible with the catalyst used in accordance with the invention overall higher yields of total C_3 unsaturate production is obtained at sufficiently high conversion levels and with marked improvement in selectivity. These high yields of C_3 unsaturates are not duplicated within the practical range of space rates by lowering the temperatures of the operation with the compared commercial catalyst.

EXAMPLE VIII

A series of runs was carried out under adiabatic conditions and at an absolute pressure of 127 mm Hg., employing the catalyst

of the previous example, at 1.5 volumes hourly space rate and at the temperatures given in Table 6 below, with the results therein reported:

TABLE 6

| Charge — (wt. %) | 95% iC ₅ — 3.2% nC ₅ | | | | |
|-----------------------------------------------|--------------------------------------------|-------|-------|-------|-------|
| Temp. °C. | | | | | |
| Inlet | 537.8 | 551.1 | 565 | 580.6 | 590.6 |
| Avg. bed | 523.9 | 535.6 | 542.8 | 557.2 | 572.8 |
| Max. outlet | 526.7 | 542.8 | 552.2 | 575.6 | 613.3 |
| Conversion (wt. iC ₅ disappear) | 23.9 | 32.2 | 36.9 | 50.3 | 60.6 |
| Product yields (wt. % charge) | | | | | |
| iC ₅ olefins | 14.1 | 17.1 | 17.2 | 21.8 | 19.8 |
| isoprene | 5.4 | 7.8 | 9.0 | 12.4 | 17.3 |
| piperylene | 0.4 | 0.7 | 0.6 | 1.8 | 2.7 |
| coke | 0.3 | 0.5 | 0.7 | 1.1 | 3.1 |
| Total Selectivity | 80.6 | 77.3 | 71.0 | 68.0 | 61.6 |

- 10 The unusually high ratios of desired isoprene to piperylene obtained are particularly noteworthy.

of Example II in the dehydrogenation of propane and isobutane respectively are shown in Table 7 below:

15

EXAMPLE IX

The results obtained in using the catalyst

TABLE 7

| Charge | Isobutane | (508 mm Hg.) | Propane | (254 mm Hg.) |
|---------------|-----------|--------------|---------|--------------|
| Temp. °C. | 593.3 | 607.2 | 593.3 | 607.2 |
| LHSV | 0.9 | 0.9 | 0.5 | 0.5 |
| Conv. wt. % | 68 | 78 | 65 | 80 |
| Olefins wt. % | 54 | 61 | 48 | 51 |

- 20 While dehydrogenation of isobutane can be accomplished at lower temperatures than is the case with C₅ hydrocarbons or with normal butane, higher temperatures can be safely and advantageously employed to obtain desired high conversion because the isobutane is less susceptible to cracking. In general, for dehydrogenation of isobutane over the highly

active catalysts of the invention, temperatures in the range of 579.4—621.1°C. are preferred at charge rates corresponding to hourly volume (as liquid) space velocity of from about 0.5 to 2; the temperatures and space rates being correlated to obtain about 60—80% conversion of the charge. Pressure may be from about 254 mm Hg. to about atmospheric. For

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dehydrogenation of propane the same conditions generally may be employed as in the case of isobutane, the temperatures being even permitted to go somewhat higher, as up to about 635°C.

WHAT WE CLAIM IS:—

1. A method of preparing a catalyst useful for dehydrogenating C_3 to C_5 hydrocarbons, which comprises dehydrating an alumina hydrate composition containing at least 60%, preferably 70 to 100%, beta alumina trihydrate, heating the resulting dehydrated alumina with a stream of gas comprising steam to adjust the surface area thereof to the range of 100 to 200 square meters per gram, depositing chromia on the area adjusted dehydrated alumina to provide a catalyst comprising 10 to 25% Cr_2O_3 , and after incorporation of the chromia the catalyst again treating the catalyst at elevated temperature with a stream of gas comprising steam.

2. Dehydrogenation catalyst prepared by the method of claim 1.

3. A method of dehydrogenating C_3 to C_5 hydrocarbons comprising passing a charge comprising such hydrocarbons over the catalyst of claim 2.

4. The method according to Claim 3, wherein the hydrocarbons charged are C_4 or C_5 hydrocarbons or mixtures thereof and the operating conditions include: temperature in the range of 515—610°C. correlated with the hourly space rate which lies in the range of 0.5 to 4.0 such that the minimum average bed temperature of the range is 510°C. plus 11 times the space rate and the maximum average bed temperature of said range is at about 554°C. plus 14 times the space rate.

5. The method according to Claim 4, wherein said C_4 hydrocarbons include recycled butylenes.

6. The method according to Claim 3 or 4, in which the hydrocarbon charge is composed substantially of C_4 hydrocarbons including butane and the operating conditions for dehydrogenation include an average bed temperature of 527—565°C., an hourly liquid volume space rate of 1 to 2 and an absolute pressure of 210 to 280 grams per square centimeter.

7. The method according to Claim 3, in which said hydrocarbon charge consists substantially of C_5 hydrocarbons including isopentane and the dehydrogenation conditions include subatmospheric pressure and temperature in the approximate range between 510°C. + 11 SR to 540°C. + 14 SR in which SR is the hourly liquid volume space velocity.

8. The method according to Claim 3, in which said hydrocarbon charge is composed predominantly of propane and the dehydrogenation thereof is effected at temperatures in the range of 593—635°C.

9. The method according to Claim 1 of preparing a catalyst useful for dehydrogenating C_3 to C_5 hydrocarbons substantially as hereinbefore described.

10. Dehydrogenation catalyst according to Claim 2 substantially as hereinbefore described.

11. A method of dehydrogenating C_3 to C_5 hydrocarbons according to Claim 3 substantially as hereinbefore described.

For the Applicants,
MATTHEWS, HADDAN & CO.,

Chartered Patent Agents,
31—32, Bedford Street, London, W.C.2.